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## Potential Constants of the Tetracyanide Ions of Nickel, Palladium, and Platinum<sup>1</sup>

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The complexes  $M(\text{CN})_4^{2-}$ ,  $M(^{13}\text{CN})_4^{2-}$  [94%  $^{13}\text{C}$ ], and  $M(\text{C}^{15}\text{N})_4^{2-}$  [99%  $^{15}\text{N}$ ], with  $M = \text{Ni, Pd, and Pt}$ , have been prepared. From Raman studies of aqueous solutions and infrared studies of aqueous solutions and solid powders, many of the vibrational frequencies have been determined. With certain judicious constraints included, force constants for a general quadratic force field have been estimated. The results indicate that for  $\text{Pt}(\text{CN})_4^{2-}$  the Pt-C  $\sigma$  bond and Pt-CN "back"  $\pi$  bond are both stronger than for the other two metals.

Some time ago estimates of the potential constants of  $\text{Pt}(\text{CN})_4^{2-}$  and  $\text{Ni}(\text{CN})_4^{2-}$  were made from analysis of vibrational spectra. No isotope shifts were available so it was necessary to make a number of constraints in the general quadratic force field. Since that time more unique force fields have been obtained<sup>4-6</sup> for several cyanide complexes using the additional data from the vibrational frequencies of species enriched in  $^{13}\text{C}$  and species enriched in  $^{15}\text{N}$ . This paper is to report a study of the potential constants of  $\text{Ni}(\text{CN})_4^{2-}$ ,  $\text{Pd}(\text{CN})_4^{2-}$ , and  $\text{Pt}(\text{CN})_4^{2-}$  from the vibrational spectra of the normal species, the completely substituted  $^{13}\text{C}$  species, and the completely substituted  $^{15}\text{N}$  species.

### Experimental Section

Potassium cyanide enriched to 94% in  $^{13}\text{C}$  was prepared from  $^{13}\text{CH}_4$  and  $\text{NH}_3$  by the method of Baufl, *et al.*,<sup>7</sup> as modified by Goldblatt and Swanson.<sup>8</sup> Similarly potassium cyanide enriched to 99% in  $^{15}\text{N}$  was prepared from  $\text{CH}_4$  and  $^{15}\text{NH}_3$ . We are grateful to W. J. McCreary of this laboratory for supplying us with  $^{13}\text{CH}_4$  and to M. Alei of this laboratory for supplying us with  $^{15}\text{NH}_3$ .

**Preparation of Complexes.** The normal and isotopically enriched (94% in  $^{13}\text{C}$  or 99% in  $^{15}\text{N}$ ) tetracyanometalates  $\text{K}_2\text{M}(\text{C}^{14}\text{N})_4$ ,  $\text{K}_2\text{M}(\text{C}^{13}\text{N})_4$ , and  $\text{K}_2\text{M}(\text{C}^{15}\text{N})_4$  were prepared by dissolving the metal dicyanide in aqueous potassium cyanide, for  $M = \text{Ni, Pd}$ . Typically, aqueous solutions of metal dichloride (1 mmol) and  $\text{K}^{12}\text{C}^{14}\text{N}$ ,  $\text{K}^{13}\text{C}^{14}\text{N}$ , or  $\text{K}^{12}\text{C}^{15}\text{N}$  (2 mmol) were mixed and the resulting precipitate of metal dicyanide was filtered off and allowed to react with 2 mmol of the appropriate KCN species in 3 ml of water. The volume of the solution was reduced to 1 ml by careful evaporation on a hot plate, 4 ml of absolute ethanol was slowly added, and the mixture was cooled to  $0^\circ$ . Fine, needlelike crystals of the tetracyanometalate formed and were filtered off and washed with ethanol. The nickel salts were anhydrous and the palladium analogs were found to be monohydrates.

The tetracyanoplatinites were prepared by fractional crystallization of an aqueous solution formed by mixing  $\text{K}_2\text{PtCl}_4$  (1 mmol) and KCN (4 mmol) in a minimum quantity of water. The tetracyanoplatinites are much less soluble at  $0^\circ$  than KCl and are readily crystallized and isolated as trihydrates. Two crystallizations were necessary to give a pure product.

**Recording of Spectra.** Raman spectra of the aqueous tetracyanometalates were recorded on a Cary Model 82 equipped with Coherent Radiation Model 52 argon and krypton lasers. A Perkin-Elmer 521 was used to obtain infrared spectra of Nujol mulls of  $\text{K}_2\text{M}(\text{CN})_4$  species in the  $4000\text{--}250\text{-cm}^{-1}$  region and of aqueous solutions in the CN stretch region. To observe the combinations of CN stretches in the  $4000\text{--}7000\text{-cm}^{-1}$  region, a Cary Model 14 was used to record

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spectra of samples dissolved in  $\text{D}_2\text{O}$  which reduces the solvent absorption in this region.

### Assignment of Frequencies

The observed frequencies are listed in Tables I and II. The  $\text{M}(\text{CN})_4^{2-}$  ions possess  $D_{4h}$  symmetry and, thus, will have 16 fundamental vibrations (2  $A_{1g}$ , 1  $A_{2g}$ , 2  $B_{1g}$ , 2  $B_{2g}$ , 1  $E_g$ , 2  $A_{2u}$ , 2  $B_{2u}$ , and 4  $E_u$ ). Of these,  $A_{2u}$  and  $E_u$  are infrared active only, while  $A_{1g}$ ,  $B_{1g}$ ,  $B_{2g}$ , and  $E_g$  are Raman active only. The  $A_{2g}$  and  $B_{2u}$  vibrations are inactive. The numerical ordering of frequencies is the same as that used earlier.<sup>2,3</sup> No  $B_{2g}$  modes were observed.

$A_{1g}$ . The  $A_{1g}$  CN and MC stretches,  $\nu_1$  and  $\nu_2$ , are readily assigned from polarization data (Table I).

$B_{1g}$ . The  $B_{1g}$  CN stretching vibration,  $\nu_4$ , is observed as a depolarized Raman frequency (Table I). The  $B_{1g}$  MC stretching vibration is obscured by the  $A_{1g}$  MC stretch. However, it is brought out when the  $A_{1g}$  mode is eliminated by  $z(xz)y$  polarization. This is analogous to the cases of  $\text{Au}(\text{CN})_4^-$ ,<sup>9</sup> with Raman shifts at 461 (p) and 452 (d)  $\text{cm}^{-1}$ , and  $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$ ,<sup>10</sup> with Raman shifts at 463 (p) and 455 (d)  $\text{cm}^{-1}$ . However, the  $B_{1g}$  bands are very weak and broad in this case. Consequently their positions could not be measured with a high degree of accuracy, and, in the case of  $\text{Pt}(\text{C}^{13}\text{N})_4^{2-}$ , this mode could not be observed at all.

$E_u$ . The strong CN stretch observed in the infrared spectra of aqueous solutions of  $\text{M}(\text{CN})_4^{2-}$  is obviously  $\nu_8$  of  $E_u$  symmetry. For mineral oil mulls of  $\text{K}_2\text{Ni}(\text{CN})_4$ , three infrared bands are observed in the  $300\text{--}600\text{-cm}^{-1}$  region. Previous studies<sup>3</sup> of the spectrum of solid  $\text{Na}_2\text{Ni}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$  indicate that the  $540.9\text{-cm}^{-1}$  band is  $\nu_9$  and the frequency pair  $421.8, 415.9\text{ cm}^{-1}$  is  $\nu_{10}$ . The  $443.7\text{-cm}^{-1}$  band ( $\nu_{12}$ ) belongs to  $A_{2u}$  symmetry. Similar assignments were made for the palladium and platinum species. We were unable to observe these midfrequency modes in aqueous solution. Therefore, as with  $\text{Co}(\text{CN})_6^{3-}$ ,<sup>6</sup> we rely on the solid-state frequencies for estimation of potential constants. This is justified by the close agreement of solid-state frequencies (Table II) and aqueous solution frequencies (Table I). The remaining  $E_u$  vibration,  $\nu_{11}$ , was not observed but should be near  $100\text{ cm}^{-1}$ .

$E_g$ . The low-frequency Raman mode is in all probability the  $E_g$  mode,  $\nu_{16}$ . The observed isotope shifts agree well with the calculated values (Table III).

### Calculation of Force Constants

The  $A_{1g}$ ,  $B_{1g}$ ,  $E_u$ , and  $E_g$  symmetry force constants were calculated by the GF-matrix method. The symmetry coordinates and internal coordinates are defined in ref 3. Anharmonic corrections identical with those used for  $\text{Co}(\text{CN})_6^{3-}$ <sup>6</sup>

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Table I. Observed Vibrational Frequencies<sup>a</sup> of Aqueous  $M(^kC^lN)_4^{2-}$ 

Assignment	M = Ni			M = Pd			M = Pt			Intens <sup>b</sup>
	<i>k, l</i>			<i>k, l</i>			<i>k, l</i>			
	12, 14	12, 15	13, 14	12, 14	12, 15	13, 14	12, 14	12, 15	13, 14	
$\nu_1$	2143.5 ± 0.2 <sup>c</sup>	2113.5	2096.5	2160.5	2130.7	2113.1	2168.0	2137.9	2119.0	s, p
$\nu_4$	2134.5 ± 0.2	2104.7	2087.8	2146.4	2116.8	2099.7	2148.8	2119.1	2100.7	vs
$\nu_2$	408.4 ± 1	401.3	401.5	428.0	420.0	423.7	469.7	462.6	466.2	w, p
$\nu_5$	410.7 ± 2	404.9	405.6	427.6	416.8	419.0	463.4	460.6		vw, b
$\nu_{16}$	300.7 ± 0.5	297.6	292.2	294.0	290.4	285.2	321.1	318.1	311.3	w
$\nu_1 + \nu_8$ <sup>d</sup>	4265.3 ± 0.5			4293.3			4297.1			w
	( $X_{18} = -1.7$ ) <sup>e</sup>			( $X_{18} = -3.0$ )			( $X_{18} = -4.3$ )			
$\nu_4 + \nu_8$ <sup>d</sup>	4239.4 ± 0.5			4264.6			4264.4			w
	( $X_{48} = -18.6$ ) <sup>e</sup>			( $X_{48} = -17.6$ )			( $X_{48} = -17.8$ )			
$\nu_8$	2123.5 ± 0.3	2092.8	2077.3	2135.8	2104.8	2089.7	2133.4	2102.5	2087.2	vs

<sup>a</sup> Units are  $\text{cm}^{-1}$ .  $\nu_8$ ,  $\nu_1 + \nu_8$ , and  $\nu_4 + \nu_8$  were observed in absorption; the other frequencies are Raman emissions. <sup>b</sup> Key: s, strong; m, medium; w, weak; b, broad; v, very; p, polarized. <sup>c</sup> Within each row, all frequencies have approximately the same error brackets as that given for  $\text{Ni}(\text{CN})_4^{2-}$ . <sup>d</sup> Observed for  $\text{D}_2\text{O}$  solutions, using a Cary 14 spectrometer. <sup>e</sup>  $X_{18} = (\nu_1 + \nu_8)_{\text{obsd}} - \nu_1 - \nu_8$ ;  $X_{48} = (\nu_4 + \nu_8)_{\text{obsd}} - \nu_4 - \nu_8$ .

Table II. Vibrational Frequencies for Solid  $\text{K}_2\text{M}(^kC^l\text{N})_4 \cdot x\text{H}_2\text{O}$ 

Assignment	M = Ni, $x = 0$			M = Pd, $x = 1$			M = Pt, $x = 3$		
	<i>k, l</i>			<i>k, l</i>			<i>k, l</i>		
	12, 14	12, 15	13, 14	12, 14	12, 15	13, 14	12, 14	12, 15	13, 14
$\nu_1$ <sup>a</sup>	2142.3 ± 0.3 <sup>d</sup>	2112.4	2095.9	2159.0			2164.6	2135.2	2115.7
$\nu_2$ <sup>a</sup>	405.5 ± 0.6	398.5	399.4	424.5			466.8	457.9	461.0
$\nu_3$ <sup>a</sup>	2133.7 ± 0.3	2104.1	2087.0	2146.8			2145.1	2115.7	2096.2
$\nu_4$ <sup>a</sup>	~415 ± 2	~407.5	~409.5						
$\nu_8$ <sup>b</sup>	{ 2126.7 ± 0.5 2121.3 ± 0.5 }	{ 2098.0 2091.2 }	{ 2081.4 } <sup>c</sup> { 2074.8 }	2134.0	2103.0	2088.0	{ 2134.0 2123.0 }	{ 2102.3 2093.7 }	{ 2087.0 } <sup>c</sup> { 2077.0 }
$\nu_9$ <sup>b</sup>	{ 540.9 ± 0.6 421.8 ± 0.6 }	{ 538.4 416.7 }	{ 533.0 410.5 } <sup>c</sup>	485.1	482.7	474.1	506.1	504.4	489.8
$\nu_{10}$ <sup>b</sup>	{ 415.9 ± 0.6 443.7 ± 0.6 }	{ 411.1 442.6 }	{ 404.6 } <sup>c</sup> { 431.9 }	383.0	379.5	376.2	407.2	401.4	401.7
$\nu_{12}$ <sup>b</sup>	443.7 ± 0.6	442.6	431.9				468.1	466.2	454.8
$\nu_{16}$ <sup>a</sup>	303.0 ± 0.3	299.9	295.4	296.0			323.4	320.0	314.4

<sup>a</sup> Observed on a Cary 82 Raman spectrometer using a powder sample. <sup>b</sup> Observed in the infrared spectra for mineral oil mulls. <sup>c</sup> These peaks are split by lattice interactions. <sup>d</sup> Within each row, all frequencies have approximately the same error brackets as that given for  $\text{K}_2\text{Ni}(\text{CN})_4$ .

were applied to the CN stretches on the basis of similar  $X_{ij}$  values calculated from the observed CN combination bands (Table I). The weights used in the calculations are the squares of the reciprocals of the estimated errors listed in Tables I and II. The same error limits were used for  $\omega_1$ ,  $\omega_4$ , and  $\omega_8$  as for the corresponding  $\nu_i$ . The absolute uncertainty in these  $\omega_i$  is much greater due to uncertainty in anharmonic corrections; however, the isotope shifts are more important than the absolute frequency values and are known with essentially the accuracy of the  $\nu_i$ .

It was necessary to constrain several of the force constants in the  $E_u$  block in order that consistent solutions be obtained for all three metals.  $F_{8,10}$  and  $F_{8,11}$  were fixed at zero as they are essentially indeterminate and the solution of the other force constants is quite insensitive to these two since the corresponding G-matrix elements are zero. A third constraint is necessary as we do not have observed values for  $\nu_{11}$ , the low-frequency CMC bending mode. It would not be appropriate to try to assign this on the basis of solid-state spectra since the shifts due to lattice interaction may be quite large.<sup>11</sup> The corresponding force constant for  $\text{Co}(\text{C}_6\text{N})_6^{3-}$  was found<sup>6</sup> to be  $\sim 0.64$  mdyne  $\text{\AA}^{-2}$ . Since the vibration is rather similar for the square-planar ions  $\text{M}(\text{CN})_4^{2-}$ , we shall constrain this constant to 0.65 mdyne  $\text{\AA}^{-2}$ .

With these three constraints we arrive at the solutions shown in Table IV. However, they are not consistent with each other or with results on other species. First, we note that  $F_{10,10}$  for Pd is much higher than that for Ni and Pt. Yet  $F_{16,16}$  (Table V) is about equal for Ni and Pd but some-

what higher for Pt and we expect the same trend for  $F_{10,10}$ , since both force constants involve MCN bends. Second,  $F_{\text{MC,CMC}}^{\text{Eu}}(F_{9,11})$  appears to be much too high by comparison with  $F_{\text{MC,CMC}}^{\text{Eu}}$  of  $\text{Co}(\text{CN})_6^{3-}$  ( $-0.2$ )<sup>6</sup> and  $\text{Cr}(\text{CO})_6$  ( $-0.3$ ).<sup>12</sup> From the symmetry force constant expressions for  $F_{\text{MC,CMC}}^{\text{Eu}}(D_{4h})$  and  $F_{\text{MC,CMC}}^{\text{Eu}}(O_h)$  we expect the former to be somewhat the smaller of the two. Therefore, we shall compromise and fix  $F_{\text{MC,CMC}}^{\text{Eu}}(F_{9,11})$  at  $-0.2$  mdyne  $\text{radian}^{-1}$ .

With these four constraints we get a reasonably good solution for the Ni complex with  $F_{10,10} = 0.35$ ; however, it is 0.57 for Pd and 0.34 for Pt. As mentioned above, the  $E_g$  frequencies suggest that  $F_{10,10}$  should be the same for Ni and Pd and somewhat higher for Pt. Thus, we shall make one further constraint:  $F_{10,10}(\text{Pd}) = F_{10,10}(\text{Ni}) = F_{10,10}(\text{Pt}) - 0.05$ . We shall accept the value of 0.35 found for  $F_{10,10}(\text{Ni})$ . The final results are given in Table V.

## Discussion

**Results of Normal-Coordinate Calculations.** The agreement of calculated and observed frequencies (Table III) is very good for all CN stretches. The agreement of MC stretches is good for the  $E_u$  modes and the  $A_{1g}$  mode of  $\text{Ni}(\text{CN})_4^{2-}$  but rather poor for the remaining  $A_{1g}$  and  $B_{1g}$  modes. The reasons for this are not entirely clear to us. The bands are quite broad, and perhaps it is too optimistic to hope to determine the MC stretches to better than  $2 \text{ cm}^{-1}$ . In addition, the  $A_{1g}$  and  $B_{1g}$  MC modes are virtually superimposed upon one another, adding further uncertainty to the peak positions.

Particularly disturbing is the isotopic shift from the normal

**Table III.** Observed Fundamental Frequencies<sup>a</sup> of  $M(\text{CN})_4^{2-}$

	$\text{Ni}(\text{C}^{13}\text{N})_4^{2-}$			$\text{Pd}(\text{C}^{13}\text{N})_4^{2-}$			$\text{Pt}(\text{C}^{13}\text{N})_4^{2-}$		
	12, 14	13, 14	<i>k, l</i>	12, 15	13, 14	<i>k, l</i>	12, 15	13, 14	<i>k, l</i>
$\omega_1^b$	2163.9 (-0.3) <sup>c</sup>	2116.2 (0.1)		2150.7 (0.2)	2132.8 (0.2)		2188.7 (0.2)	2138.7 (-0.1)	
$\nu_2^b$	408.4 (-0.4)	401.6 (-0.1)		420.0 (-0.7)	423.7 (1.9)		469.7 (-2.3)	466.2 (2.2)	
$\omega_3^b$	2154.8 (-0.3)	2107.3 (0.2)		2136.7 (0.3)	2119.3 (0.2)		2169.3 (-0.1)	2120.3 (0.0)	
$\nu_4^b$	410.7 (-1.5)	405.6 (0.6)		416.8 (-1.2)	419.0 (0.0)		463.4 (-3.2)	[458.6] <sup>e</sup>	
$\omega_5^b$	2143.7 (-0.1)	2096.7 (0.1)		2124.6 (-0.1)	2109.2 (-0.1)		2153.7 (-0.1)	2106.7 (0.0)	
$\nu_6^b$	540.9 (-0.2)	533.0 (0.1)		482.7 (-0.4)	474.1 (0.3)		506.1 (-0.2)	489.8 (0.0)	
$\nu_{10}$	418.8 <sup>d</sup> (0.5)	407.5 <sup>d</sup> (-0.1)		379.5 (-0.1)	376.2 (0.6)		407.2 (-0.2)	401.7 (-0.1)	
$\nu_{11}$	[102.4] <sup>e</sup>	[101.9]		[90.4]	[90.0]		[77.6]	[77.3]	
$\nu_{16}$	300.7 (0.0)	292.2 (0.4)		290.4 (1.4)	285.2 (-0.3)		321.1 (0.0)	311.3 (-0.5)	

<sup>a</sup> Units are  $\text{cm}^{-1}$ . <sup>b</sup> Frequencies listed here as  $\omega_i$  include anharmonic corrections. <sup>c</sup> Numbers in parentheses are observed minus calculated frequencies using the force constants of Table IV. <sup>d</sup> Average value of frequency pair listed in Table II. <sup>e</sup> Numbers in brackets are values calculated from force constants of Table V.

**Table IV.** Initial  $E_u$  Symmetry Force Constants<sup>a</sup>

	$\text{Ni}(\text{CN})_4^{2-}$	$\text{Pd}(\text{CN})_4^{2-}$	$\text{Pt}(\text{CN})_4^{2-}$
$F_{8,8}(\text{CN})$	17.05 (11) <sup>b</sup>	17.35 (8)	17.38 (6)
$F_{9,9}(\text{MC})$	1.66 (25)	1.63 (22)	1.96 (13)
$F_{10,10}(\text{MCN})$	0.30 (13)	0.51 (14)	0.31 (9)
$F_{11,11}(\text{CMC})$	[0.65] <sup>c</sup>	[0.65]	[0.65]
$F_{8,9}$	0.06 (15)	0.13 (13)	0.28 (8)
$F_{8,10}$	[0]	[0]	[0]
$F_{8,11}$	[0]	[0]	[0]
$F_{9,10}$	0.26 (26)	0.10 (28)	0.21 (19)
$F_{9,11}$	0.57 (47)	-0.51 (63)	-0.44 (57)
$F_{10,11}$	0.13 (13)	-0.08 (14)	0.31 (9)
$\nu_{11}(\text{C}^{14}\text{N})(\text{calcd})$	56.9	97.1	34.1

<sup>a</sup> Units are  $\text{mdyn } \text{Å}^{-1}$  for stretching constants,  $\text{mdyn } \text{Å radian}^{-2}$  for bending constants,  $\text{mdyn radian}^{-1}$  for stretch-bends, and  $\text{cm}^{-1}$  for  $\nu_{11}$ . <sup>b</sup> Numbers in parentheses are standard deviations in the last digit given for the constant. <sup>c</sup> Terms in brackets were constrained for reasons described in the text.

**Table V.** Final Symmetry Force Constants<sup>a</sup>

	$\text{Ni}(\text{CN})_4^{2-}$	$\text{Pd}(\text{CN})_4^{2-}$	$\text{Pt}(\text{CN})_4^{2-}$
$A_{1g}$			
$F_{1,1}(\text{CN})$	17.40 (7) <sup>b</sup>	17.56 (10)	17.53 (7)
$F_{2,2}(\text{MC})$	2.63 (1)	2.92 (3)	3.56 (2)
$F_{1,2}$	0.32 (6)	0.29 (9)	0.33 (6)
$B_{1g}$			
$F_{4,4}(\text{CN})$	17.21 (9)	17.43 (12)	17.32 (11)
$F_{5,5}(\text{MC})$	2.68 (2)	2.87 (3)	3.46 (4)
$F_{4,5}$	0.30 (8)	0.37 (11)	0.41 (9)
$E_u$			
$F_{8,8}(\text{CN})$	17.10 (7)	17.37 (9)	17.39 (4)
$F_{9,9}(\text{MC})$	1.84 (3)	1.74 (3)	1.99 (2)
$F_{10,10}(\text{MCN})$	0.35 (9)	[0.35] <sup>c</sup>	[0.40]
$F_{11,11}(\text{CMC})$	[0.65]	[0.65]	[0.65]
$F_{8,9}$	0.15 (6)	0.18 (8)	0.30 (4)
$F_{8,10}$	[0]	[0]	[0]
$F_{8,11}$	[0]	[0]	[0]
$F_{9,10}$	0.07 (3)	0.02 (1)	0.15 (4)
$F_{9,11}$	[-0.2]	[-0.2]	[-0.2]
$F_{10,11}$	0.08 (10)	0.12 (1)	0.22 (1)
$E_g$			
$F_{16,16}(\text{MCN})$	0.24	0.24	0.29

<sup>a</sup> Units are  $\text{mdyn } \text{Å}^{-1}$  for all stretching force constants and stretch-stretch interactions ( $F_{1,1}, F_{2,2}, F_{1,2}, F_{4,4}, F_{5,5}, F_{4,5}, F_{8,8}, F_{9,9}, F_{8,9}$ ). The units are  $\text{mdyn } \text{Å radian}^{-2}$  for the bends ( $F_{16,16}, F_{10,10}, F_{11,11}, F_{10,11}$ ). For the stretch-bend interactions ( $F_{8,10}, F_{8,11}, F_{9,10}$ , and  $F_{9,11}$ ) the units are  $\text{mdyn radian}^{-1}$ . The bond lengths used in the calculations are 1.13 Å for  $r_{\text{CN}}$  and 1.86 Å for  $r_{\text{MC}}$  as found for  $\text{K}_2\text{-Ni}(\text{CN})_4$  [see N. Vannerberg, *Acta Chem. Scand.*, 18, 2385 (1964)]; 1.16 Å for  $r_{\text{CN}}$  and 2.00 Å for  $r_{\text{MC}}$  as found for  $\text{Na}_3\text{Pd}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$  and 1.11 Å for  $r_{\text{CN}}$  and 2.02 Å for  $r_{\text{MC}}$ , average values for a series of  $\text{Pt}(\text{CN})_4^{2-}$  salts [see M. L. Colin-Moreau, *Struct. Bonding (Berlin)*, 10, 167 (1972), for Pd and Pt compounds]. <sup>b</sup> Numbers in parentheses are standard deviations in the last digit given for the constant. <sup>c</sup> Terms in brackets were constrained for reasons described in the text.

**Table VI.** Bond Stretching Force Constants<sup>a</sup>

	$\text{Ni}(\text{CN})_4^{2-}$	$\text{Pd}(\text{CN})_4^{2-}$	$\text{Pt}(\text{CN})_4^{2-}$	$\text{Co}(\text{CN})_6^{3-}$
$F_{\text{CN}}$	17.20 (5) <sup>b</sup>	17.44 (6)	17.41 (4)	17.43 <sup>c</sup>
$F_{\text{CN}}^c, \text{C}'\text{N}'$	0.05 (3)	0.03 (4)	0.05 (3)	0.07
$F_{\text{CN}}^d, \text{C}'\text{N}'$	0.10 (5)	0.06 (6)	0.02 (4)	-0.07
$F_{\text{MC}}$	2.25 (2)	2.32 (2)	2.75 (1)	2.09
$F_{\text{MC}}^c, \text{M}'\text{C}'$	-0.01 (1)	0.01 (1)	0.03 (1)	0.02
$F_{\text{MC}}^d, \text{M}'\text{C}'$	0.41 (2)	0.58 (2)	0.76 (1)	0.45
$F_{\text{MC}, \text{CN}}$	0.23 (5)	0.25 (5)	0.34 (3)	0.24
$F_{\text{MC}}^c, \text{C}'\text{N}'$	0.01 (3)	-0.02 (3)	-0.02 (3)	0.02
$F_{\text{MC}}^d, \text{C}'\text{N}'$	0.08 (5)	0.07 (5)	0.04 (3)	0.10

<sup>a</sup> Units are  $\text{mdyn } \text{Å}^{-1}$ . <sup>b</sup> Numbers in parentheses are least-squares standard deviations in the last digit given for the constant. <sup>c</sup> The  $\text{Co}(\text{CN})_6^{3-}$  constants are from ref 6.

species to the  $^{13}\text{C}$  species for the  $A_{1g}$  MC stretches of  $\text{Pt}(\text{CN})_4^{2-}$  ( $\Delta\nu_{\text{obsd}} = 3.5 \text{ cm}^{-1}$ ;  $\Delta\nu_{\text{calcd}} = 8.0 \text{ cm}^{-1}$ ) and  $\text{Pd}(\text{CN})_4^{2-}$  ( $\Delta\nu_{\text{obsd}} = 4.3 \text{ cm}^{-1}$ ;  $\Delta\nu_{\text{calcd}} = 7.4 \text{ cm}^{-1}$ ). The CN stretches fix the force field rather well, and it is not possible to fit the MC stretches even if they are weighted more heavily than

the CN stretches. Discrepancies in isotope shifts for MC stretching modes have been observed previously though to a lesser extent. In this case the deviations are well outside experimental error and must arise from some perturbation we do not yet understand. The observed shifts in the solid state for the Pt compound are in much better agreement. This suggests that there may be some distortion caused by interaction with the solvent for the Pt and Pd species. Nevertheless, as mentioned above, the force field is well fixed by the CN stretches so that the results on the stretching constants are definitely significant. The use of solid-state frequencies has little effect on the calculated force constants.

In Table VI we present the internal coordinate stretching force constants for comparison among the  $M(CN)_4^{2-}$  complexes and with  $Co(CN)_6^{3-}$ . It is apparent that both the CN and MC bond strengths are greater for  $Pt(CN)_4^{2-}$  than for  $Ni(CN)_4^{2-}$ . This indicates greater  $\sigma$ -bond strength for Pt-C than for Ni-C.<sup>13</sup> Note also that  $F_{MC,CN}$  and  $F_{MC,MC}^t$  are greater for the Pt complex, as can be expected for stronger M-C bonding. The Pd complex falls in between with Pd-C more like Ni-C but  $F_{CN}(Pd)$  more like  $F_{CN}(Pt)$ . The picture is no doubt complicated by some differences in  $\pi$  bond-

ing. Intensity studies<sup>14</sup> indicate that M-CN "back"  $\pi$  bonding is greater for  $Pt(CN)_4^{2-}$  than for the other two. A comparison of intensities and force constants suggests that Pd-C has slightly greater  $\sigma$ -bond strength than Ni-C while Pt-C has greater  $\sigma$ -bond strength and greater  $\pi$ -bond strength than either of the other two species.

A comparison with  $Co(CN)_6^{3-}$  indicates that the M-C bond is weaker for the hexacyanide even though intensity studies<sup>14</sup> indicate that the Co-C  $\pi$  bonding is stronger than that for Pt-C. The comparison suggests that the M-C  $\sigma$  bond is inherently weaker for hexacyanides though its effect on strengthening the CN bond is greater. Similar studies of other metal cyanide complexes should throw further light into these interesting bonding systems.

**Registry No.**  $Ni(^{12}C^{14}N)_4^{2-}$ , 48042-08-6;  $Ni(^{12}C^{15}N)_4^{2-}$ , 52540-55-3;  $Ni(^{13}C^{14}N)_4^{2-}$ , 52540-56-4;  $Pd(^{12}C^{14}N)_4^{2-}$ , 15004-87-2;  $Pd(^{12}C^{15}N)_4^{2-}$ , 52540-57-5;  $Pd(^{13}C^{14}N)_4^{2-}$ , 52540-58-6;  $Pt(^{12}C^{14}N)_4^{2-}$ , 15004-88-3;  $Pt(^{12}C^{15}N)_4^{2-}$ , 52540-59-7;  $Pt(^{13}C^{14}N)_4^{2-}$ , 52540-60-0;  $K_2Ni(^{12}C^{14}N)_4$ , 14220-17-8;  $K_2Ni(^{12}C^{15}N)_4$ , 52540-61-1;  $K_2Ni(^{13}C^{14}N)_4$ , 52540-62-2;  $K_2Pd(^{12}C^{14}N)_4 \cdot H_2O$ , 16457-34-4;  $K_2Pd(^{12}C^{15}N)_4 \cdot H_2O$ , 52540-63-3;  $K_2Pd(^{13}C^{14}N)_4 \cdot H_2O$ , 52540-64-4;  $K_2Pt(^{12}C^{14}N)_4 \cdot 3H_2O$ , 14323-36-5;  $K_2Pt(^{12}C^{15}N)_4 \cdot 3H_2O$ , 52540-65-5;  $K_2Pt(^{13}C^{14}N)_4 \cdot 3H_2O$ , 52540-66-6.

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## Synthesis and Crystal Structure of a Polymeric Copper(I) Aliphatic Disulfide Complex. {Bis[2-(2-pyridyl)ethyl] disulfide}copper(I) Perchlorate

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{Bis[2-(2-pyridyl)ethyl] disulfide}copper(I) perchlorate, alternatively named [2,2'-(dithiodiethylene)dipyridine]copper(I) perchlorate,  $Cu(C_5H_4NCH_2CH_2SSCH_2CH_2C_5H_4N)ClO_4$ , has been synthesized by disulfide ligand reaction with Cu(II) and subsequent Cu(I) coordination with excess disulfide. Its crystal structure has been determined by single-crystal X-ray diffraction techniques. After large-block-diagonal least-squares refinement using anisotropic thermal parameters for nonhydrogen atoms and isotropic ones for hydrogens, the conventional  $R$  index converged at 0.043. The yellow crystals form in the monoclinic space group  $P2_1/c$  with  $a = 10.408$  (3) Å,  $b = 8.249$  (2) Å,  $c = 20.662$  (7) Å,  $\beta = 108.99$  (3)°, and  $Z = 4$ . Half  $(C_5H_4NCH_2CH_2S^-)$  of two different ligands is coordinated to each Cu(I) ion. This results in two six-membered chelate rings and a somewhat distorted tetrahedral coordination environment of two sulfur and two nitrogen atoms about each Cu(I). The remaining halves of each disulfide ligand associate with different Cu(I) ions, forming a cationic polymeric chain. The average Cu(I) bond distances to the sulfur and nitrogen donor atoms are 2.322 (1) and 2.029 (1) Å, respectively. The Raman shift of the S-S stretch is  $484\text{ cm}^{-1}$ , significantly less than the expected value for the uncoordinated disulfide ligand. This correlates qualitatively with the observed coordination of the disulfide moiety, the closing of the CSSC dihedral angle to  $59.7$  (1)°, and the lengthening of the S-S bond to 2.081 (1) Å. A uv band associated with the complexed disulfide appears at  $293\text{ m}\mu$ , as compared to  $248\text{ m}\mu$  in the uncoordinated ligand. A similar band at approximately  $330\text{ m}\mu$  is observed in the oxidized form of ceruloplasmin, in which the complexation of Cu(I) by disulfide has been reported.

### Introduction

In order to elucidate the role of transition metal ions in the structure and function of some metalloenzymes and metalloproteins, attempts have been made to synthesize aliphatic disulfide complexes of transition metal ions and to determine their molecular structures. A detailed introduction can be found in the reports of the first two structures determined in this laboratory: those of a Ni(II) complex,<sup>1</sup> chloro[bis-[2-[(2-pyridylmethyl)amino]ethyl] disulfide]nickel(II) perchlorate, and of a Cu(I) complex,<sup>2</sup> *cyclo*-di- $\mu$ -{bis[2-(*N,N*-

dimethylamino)ethyl] disulfide}dicopper(I) tetrafluoroborate,  $[Cu(RSSR)]_2(BF_4)_2$ .

It has recently been reported that the oxidized form of the two-electron copper oxidase ceruloplasmin, present in the  $\beta$ -globulin fraction of mammalian blood serum, has Cu(I)-complexed RSSR at its two-copper site.<sup>3</sup> Perhaps the readily prepared copper(I) organic disulfide small-molecule complexes can act as models for the corresponding active site in the large metalloprotein ceruloplasmin and in other copper oxidases as well.

Unfortunately,  $[Cu(RSSR)]_2(BF_4)_2$  is unstable, both in

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